

Tailoring Integrated Layered- and Spinel Electrode Structures for High Capacity Lithium-Ion Cells

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Argonne National Laboratory*

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DOE Vehicle Technologies Program
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ES049

Overview

Timeline

- Start date: FY16
- End date: FY18
- Percent complete: 50%

Budget

- Total project funding: 100% DOE
- FY16 Funding:
 - Composite Electrodes: \$500K
 - Spinel Components: \$500K

Barriers

- Low energy density
- Cost
- Abuse tolerance limitations

Partners

- Lead PI: Michael Thackeray, Co-PI: Jason Croy
- Collaborators:
 - CSE, Argonne: Eungje Lee, *Joong Sun Park*, Arturo Gutierrez, *Bryan Yonemoto*, Meinan He Roy Benedek, Fulya Dogan (NMR)
 - APS, Argonne: Mali Balasubramanian (XAS)
 - Northwestern University, NUANCE: Vinayak Dravid, Jinsong Wu (TEM)
 - PNNL: Chongmin Wang (TEM)
 - ORNL: Harry Meyer (XPS)
 - Industry: Argonne licensees and collaborators

Objectives

- Design and characterize high capacity, high-power, safe and low cost cathodes for PHEVs and EVs
 - Improve the structural design, composition and electrochemical performance of Mn-rich cathodes *to make them competitive with Ni-rich cathode compositions, e.g., 622*
 - Design and engineer stable electrode surfaces to improve capacity and cycle life when charged to high potentials

Milestones (FY16)

- Optimize the composition, capacity and cycling stability of structurally-integrated 'layered-layered' and 'layered-layered-spinel' cathode materials. **Target capacity = 200 mAh/g for baseline electrode achieved. Project on-going.**
- Scale up the most promising materials to batch sizes required for evaluation by industry (10g-100g-1kg). **Achieved. Project on-going.**
- Synthesize and determine the electrochemical properties of unique surface architectures that enable >200 mAh/g at a >1C rate. **Project on-going.**
- Synthesize and optimize spinel compositions and structures with a focus on Co-based systems for use in structurally-integrated 'layered-spinel' systems. **Project on-going.**

Approach

- Exploit the concept and optimize the performance of *structurally-integrated ('composite') electrode structures* with a focus on '*layered-layered-spinel*' materials.
- Design effective *surface structures* to protect the underlying metal oxide particles from the electrolyte and to improve and maintain their stability and rate capability when charged to high potentials (4.5-4.6 V).

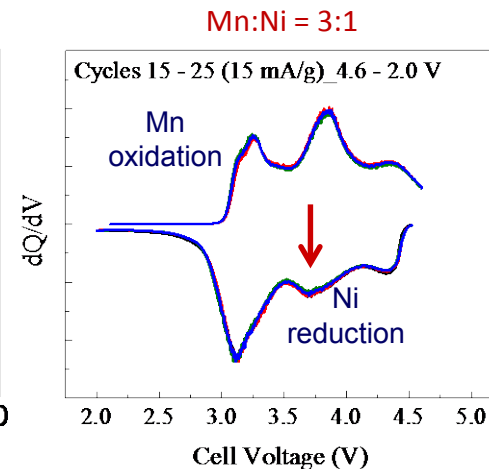
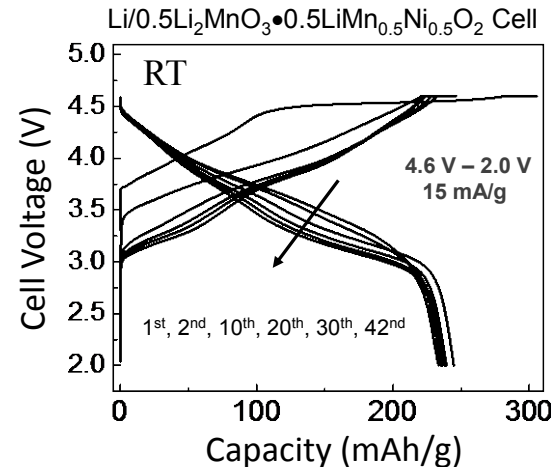
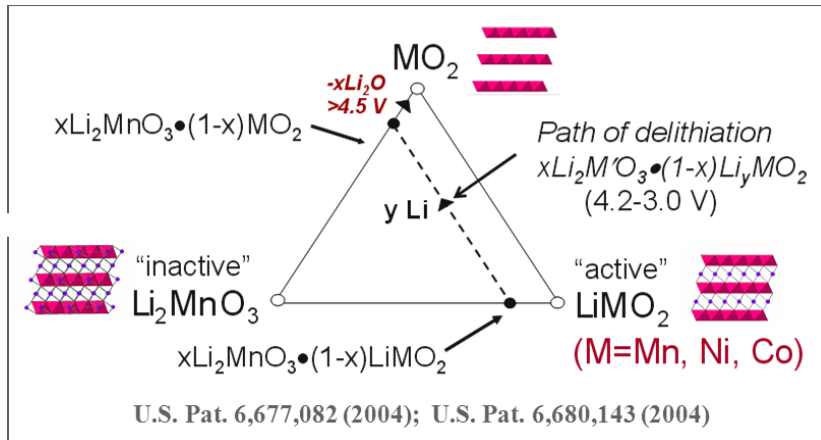
Motivation for R&D Approach

Major Materials Challenges for Li-ion Batteries

- Increase the energy density of cells – both volumetric and gravimetric for portable/mobile applications
 - Increase cell voltage
 - Increase electrode capacity ⇒ Mn rather than Co-, Ni-rich oxides
- Reduce cost and toxicity ⇒ Mn-rich rather than Co, Ni-rich cathodes
- Reduce/Eliminate Safety Hazard:
 - *Lithium Batteries Could Spark 'Catastrophic' Plane Fires, FAA Warns (2016)*
 - Control electrochemical and chemical reactions to eliminate the risks of thermal runaway
 - ⇒ Mn-rich rather than Co, Ni-rich oxide cathodes
 - ⇒ Non-flammable electrolytes
 - ⇒ Voltage control

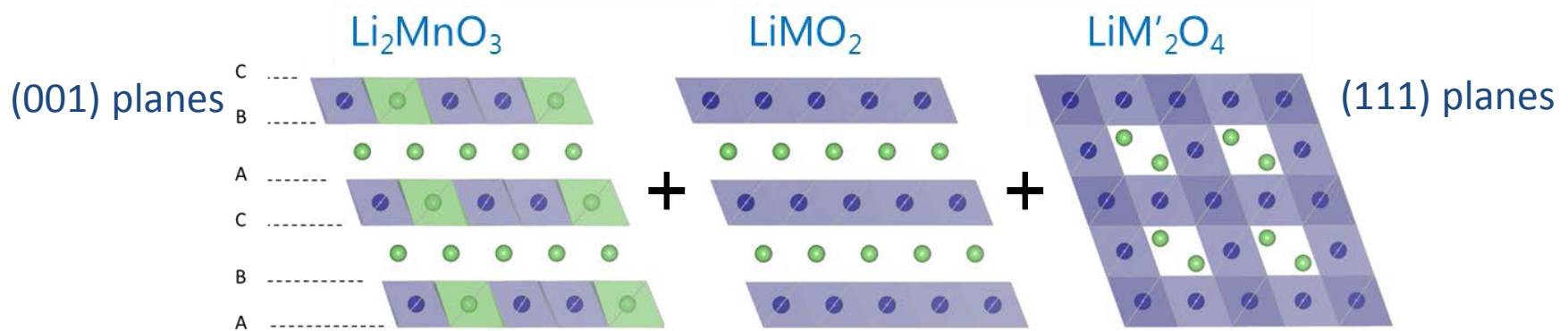
Lithium- and Manganese-Rich Composite Electrodes

- Structure – integrated nanodomains yield complex structures
- Surface stabilization – electrochemical “activation” leads to irreversible structural changes, surface damage, voltage fade, and hysteresis
- Hysteresis – energy inefficiency
- Voltage Fade – continuous decrease in energy output with cycling
– compromises battery management

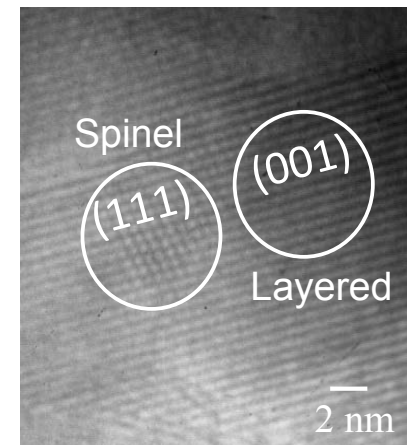
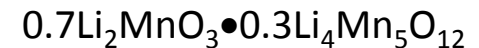


Stabilization of $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMO}_2$ Electrodes

- Extend concept of integrated structures to 'layered-layered-spinel' (LLS) systems
- Embed TM metal pillars (spinel component) to stabilize 'layered-layered' structures



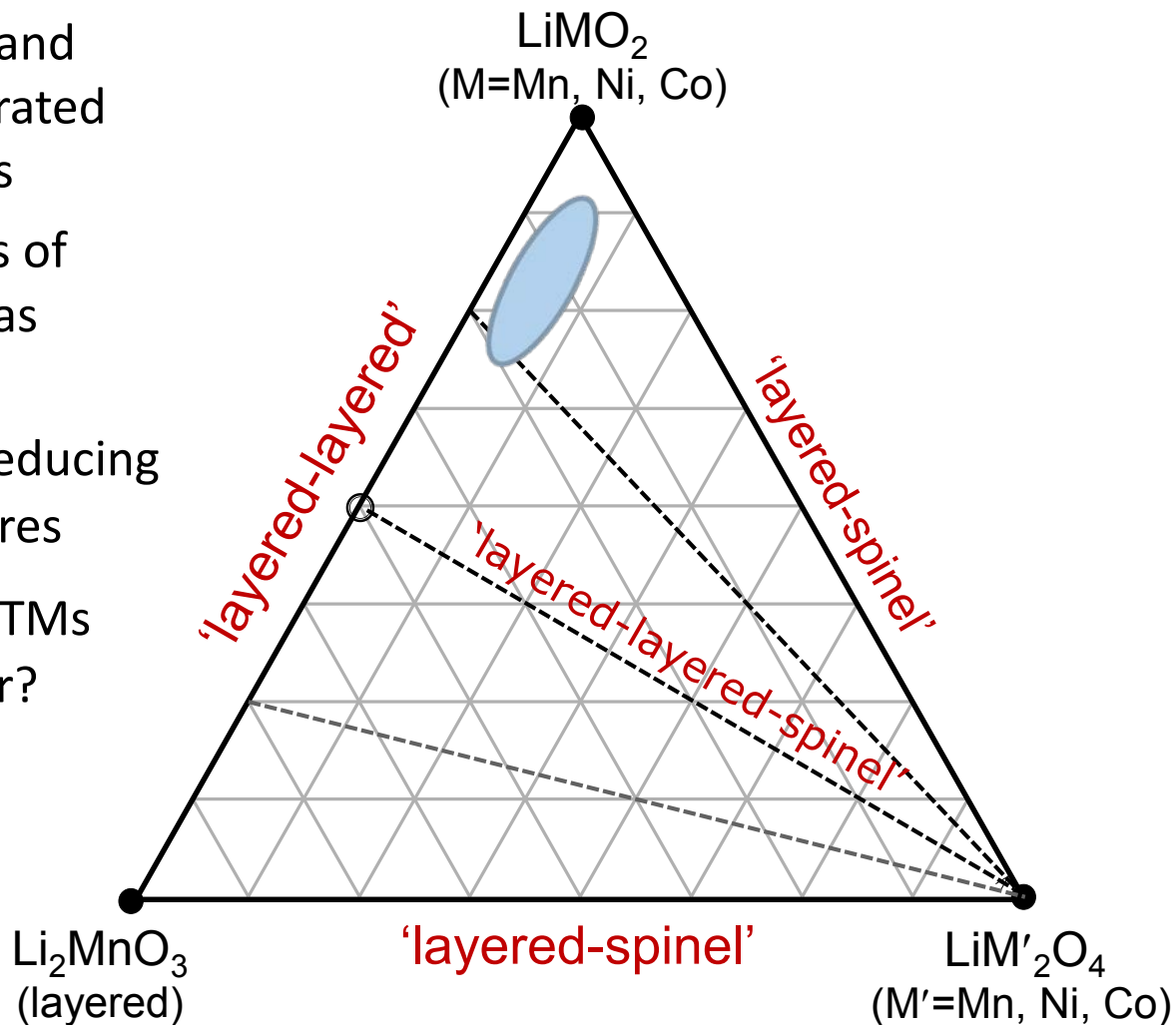
- Compatibility of cubic-close-packed planes in layered Li_2MnO_3 (001) and spinel $\text{Li}_4\text{M}_5\text{O}_{12}$ (111) allows structural integration of the two components
- Nano-composite structure



The Li_2MnO_3 – LiMO_2 – $\text{LiM}'_2\text{O}_4$ System

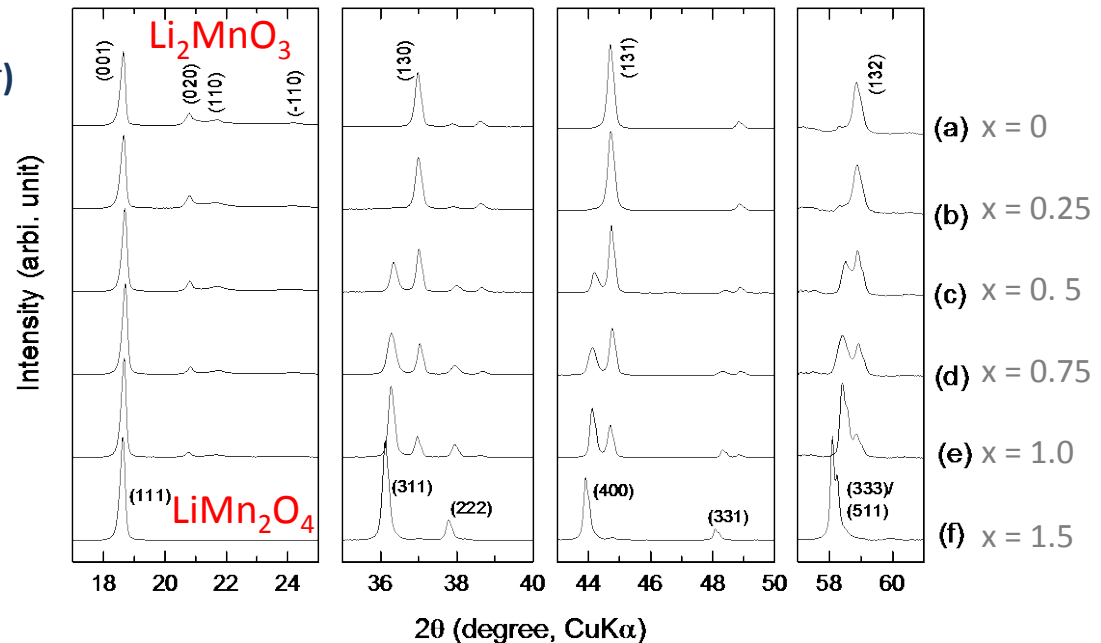
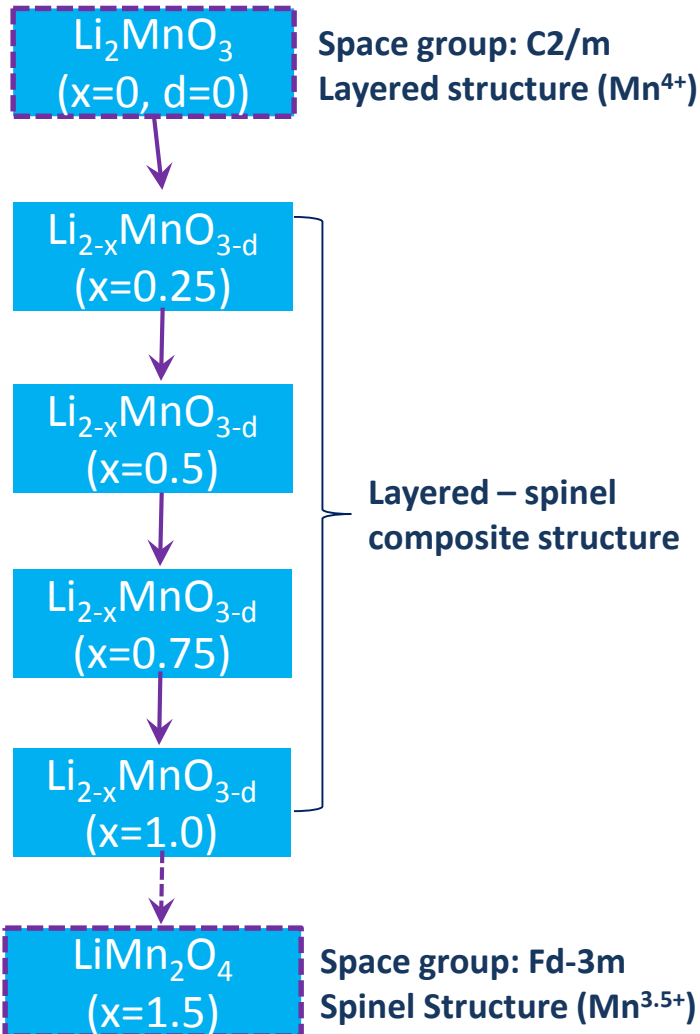
Conceptual Design Space of 'Layered-Layered-Spinel' (LLS) Electrodes

- Wide Li-M-O compositional and phase space to exploit integrated layered and spinel structures
- Use relatively small amounts of Li_2MnO_3 and $\text{LiM}'_2\text{O}_4$ spinel as stabilizers
- Spinel domains created by reducing the Li content in 'LL' structures
- At what Li concentration do TMs start migrating to the Li layer?
- Highly complex structural arrangements



Reducing Li Content in Li_2MnO_3 and LiMO_2

- Li-deficient $\text{Li}_{2-x}\text{MnO}_3$ transforms to spinel ($\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$) on heating ($\sim 850^\circ\text{C}$)

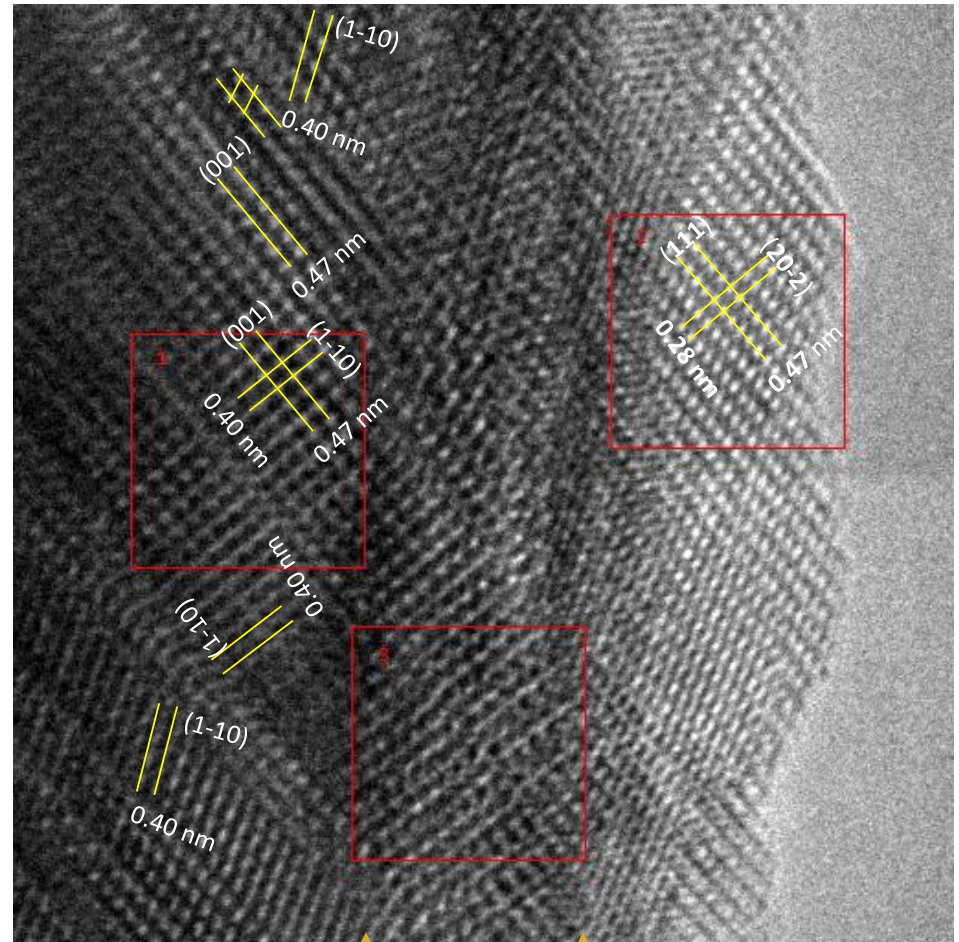


- Delithiated $\text{Li}_{1-x}\text{MO}_2$ structures, e.g., $\text{M}=\text{Ni}$, V , Mn also transform on heating to spinel:

- 1) M. Thomas, W. I. F. David, J. B. Goodenough, P. Groves, Mater. Res. Bull., **20**, 1137 (1985).
- 2) L. A. de Picciotto and M. M. Thackeray, Mater. Res. Bull., **20**, 187-195 (1985)
- 3) R. J. Gummow, D. C. Liles and M. M. Thackeray, Mater. Res. Bull., **28**, 1249 (1993).

HRTEM of ' $\text{Li}_{2-x}\text{MnO}_{3-\delta}$ ' ($x=1$)

- Structure characterized by faulted layered Li_2MnO_3 regions, and LiMn_2O_4 spinel regions that exist predominantly at the surface
- Distorted intergrown regions at the interface – mismatch in lattice parameters?



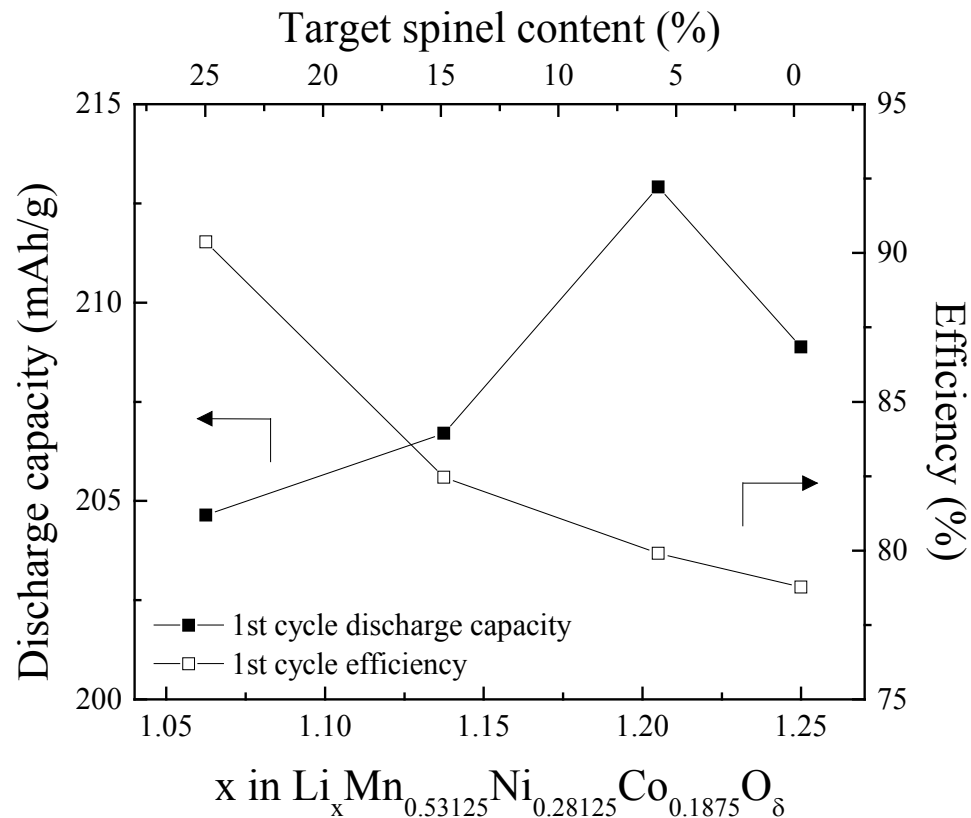
Faulted layered
structure

Distorted
intergrown
interface

Spinel phase

The Effect of Lithium Content in 'Baseline' NMC ~'532'

' $0.25\text{Li}_{2-x}\text{MnO}_{3-\delta} \bullet 0.75\text{LiMn}_{0.375}\text{Ni}_{0.375}\text{Co}_{0.25}\text{O}_2$ ' i.e., $\text{Li}_x\text{Mn}_{0.53}\text{Ni}_{0.28}\text{Co}_{0.19}\text{O}_\delta$ (Mn:Ni ~ 2:1)

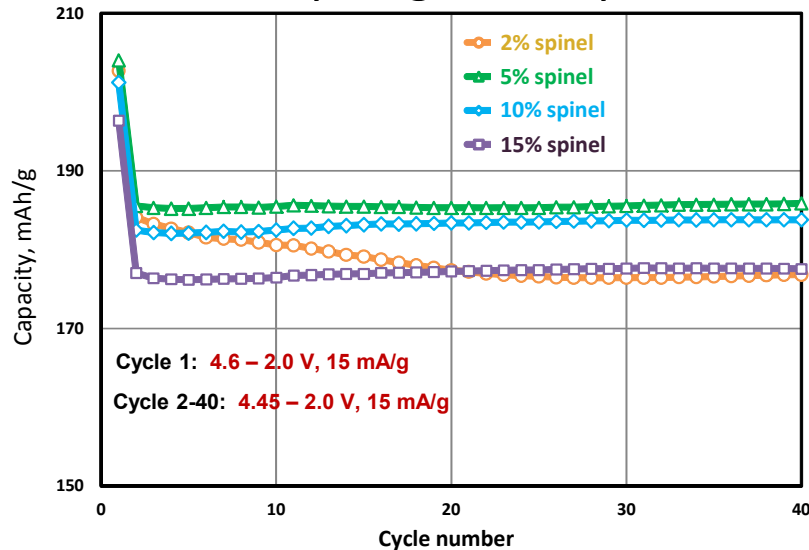


- Maximum capacity at ~6% 'targeted' spinel content
- 1st-cycle efficiency increases with increasing spinel content
- Rate capability increases – spinel-stabilized surface?

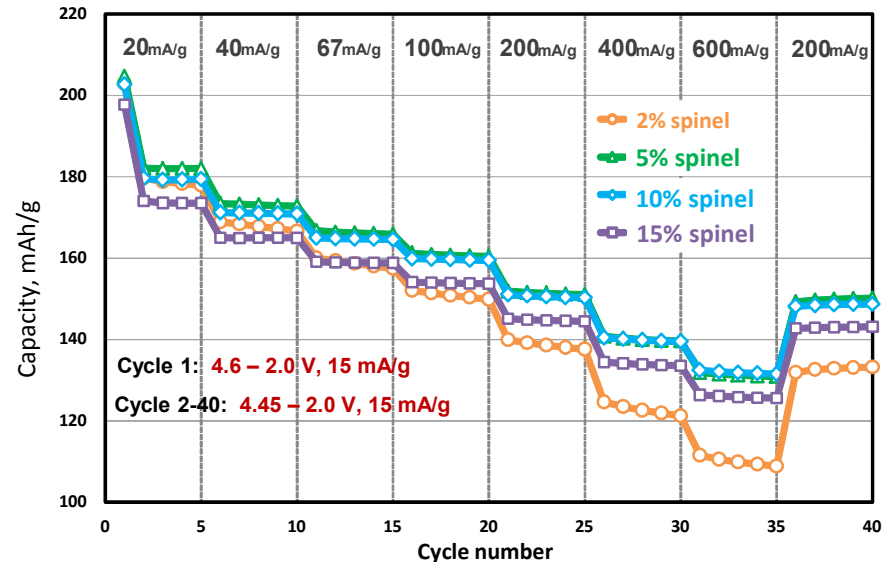
Cycling Stability and Rate Performance (4.45-2V)

MERF Facility - $\text{Li}_x\text{Mn}_{0.53}\text{Ni}_{0.28}\text{Co}_{0.19}\text{O}_\delta$

Cycling Stability



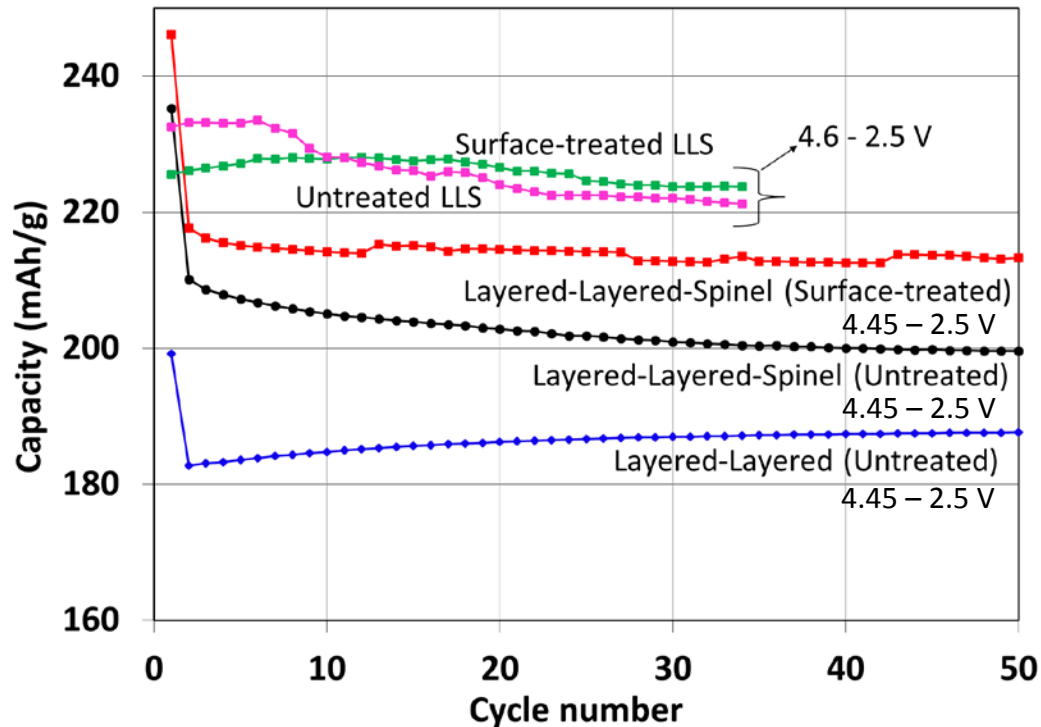
Rate Performance



- Electrodes containing 5-10% spinel (targeted amount) show significantly better capacity and rate capability relative to those with 2% and 15%
- Stable cycling
- Powders with targeted 6% spinel scaled to 800g production

Untreated and Surface-treated LL and LLS Electrodes

(derived from $0.25\text{Li}_2\text{MnO}_3 \bullet 0.75\text{LiMn}_{0.375}\text{Ni}_{0.375}\text{Co}_{0.25}\text{O}_2$; Mn:Ni ~2:1)



Cycling protocol in Li half cells:
(15 mA/g charge and discharge)

(a)

- One activation cycle: 4.60 - 2.0 V
- Subsequent cycles: 4.45 - 2.5 V
- 210-220 mAh/g

(b)

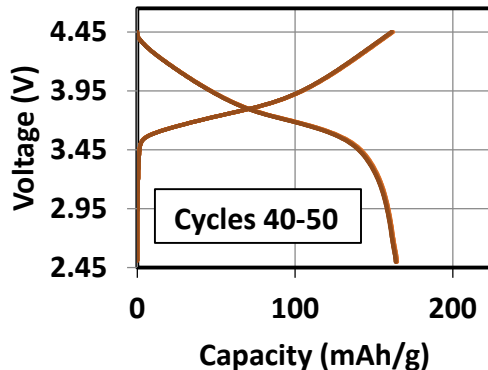
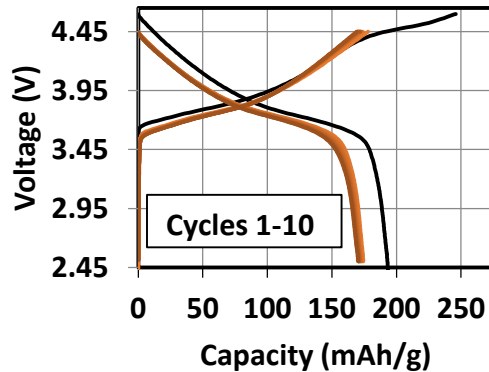
- One activation cycle: 4.60 - 2.0 V
- Subsequent cycles: 4.60 - 2.5 V
- 220-230 mAh/g

■ US Patent Application Filed

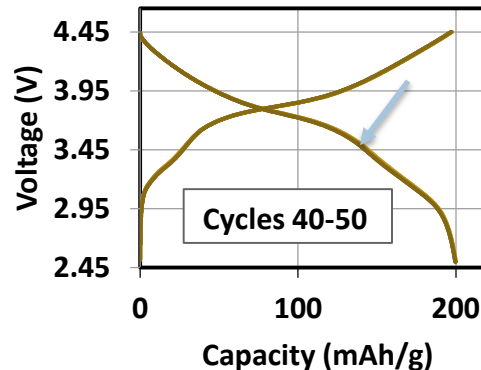
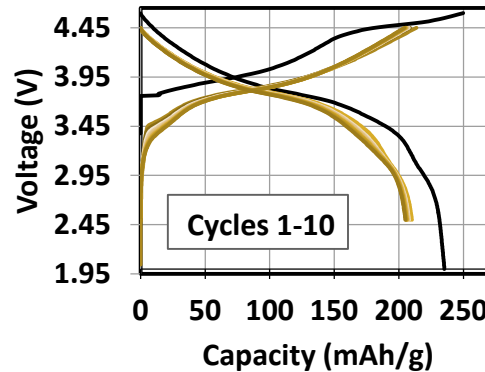
Untreated and Surface-treated LL and LLS Electrodes

(derived from $0.25\text{Li}_2\text{MnO}_3 \bullet 0.75\text{LiMn}_{0.375}\text{Ni}_{0.375}\text{Co}_{0.25}\text{O}_2$; Mn:Ni ~ 2:1)

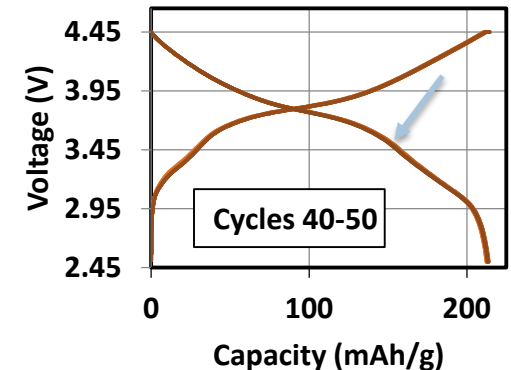
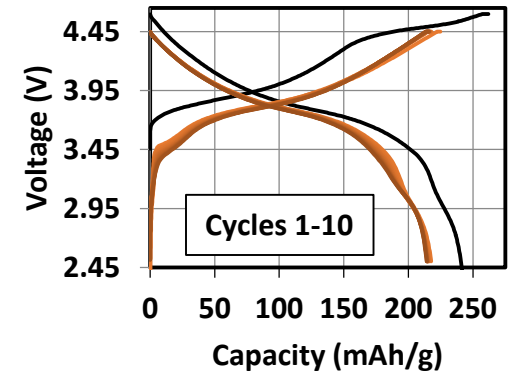
Layered-layered (LL)



Untreated LLS



Surface treated LLS

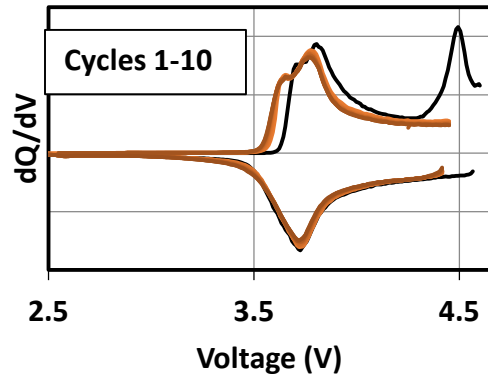


- Steady cycling after activation (voltage fade suppressed)
- 'Approaching end-of-life' indicator at ~3.5 V in LLS electrodes

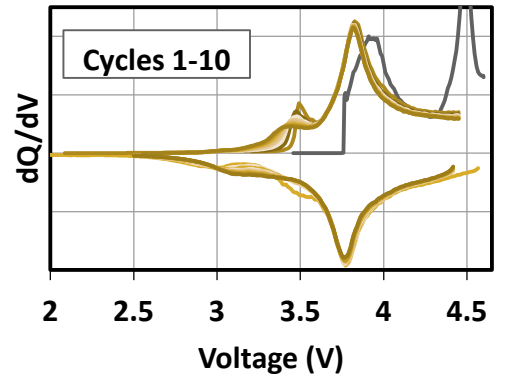
Untreated and Surface-treated LL and LLS Electrodes

(derived from $0.25\text{Li}_2\text{MnO}_3 \bullet 0.75\text{LiMn}_{0.375}\text{Ni}_{0.375}\text{Co}_{0.25}\text{O}_2$; Mn:Ni ~2:1)

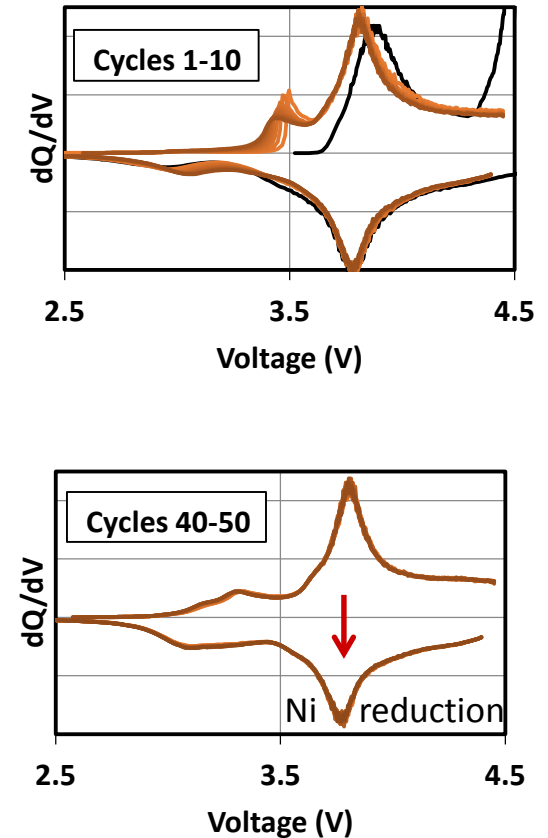
Layered-layered (LL)



Untreated LLS



Surface treated LLS



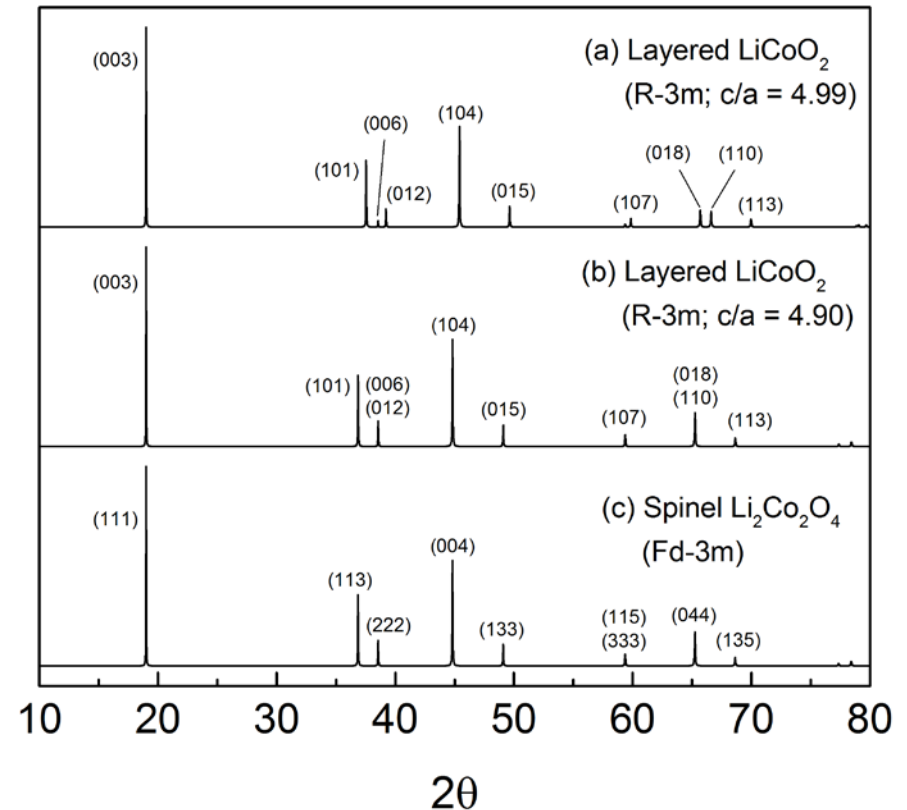
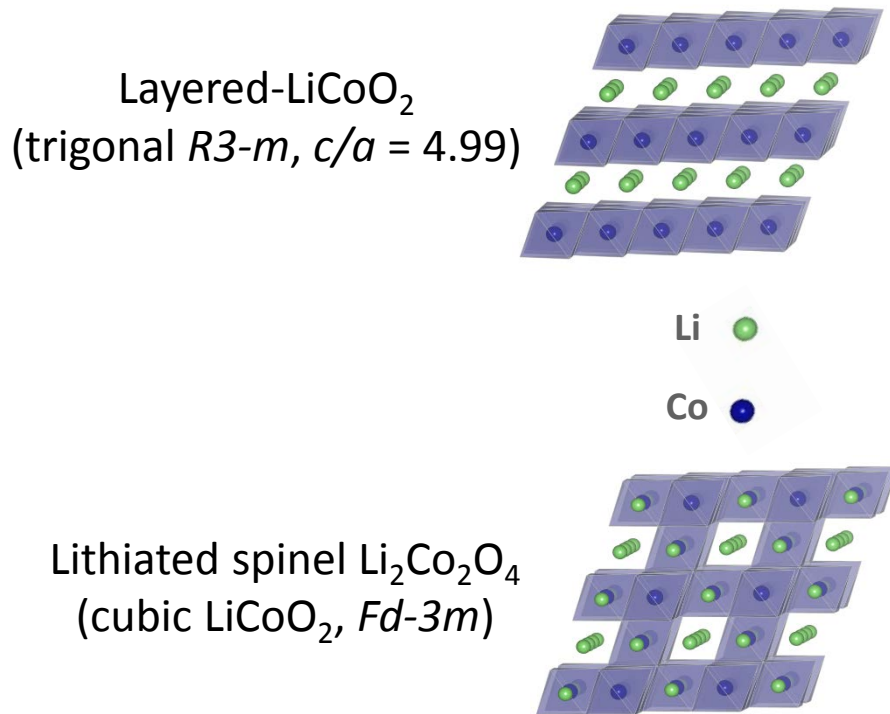
- Predominant Ni reduction peak at 3.7 V, less hysteresis than in $0.5\text{Li}_2\text{MnO}_3 \bullet 0.5\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ electrodes

LLS Electrodes with Lithium-Cobalt-Nickel-Oxide Spinel?

Embedding a lithiated cobalt-rich spinel rather than a manganese-based spinel as a stabilizer for high capacity $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ electrodes seems attractive:

- Lithiated spinels $\text{Li}_2[\text{Co}_{2-2x}\text{Ni}_{2x}]\text{O}_4$, like $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ materials have close-packed structures with a rock salt stoichiometry, making them compositionally, and potentially structurally, compatible with one another
- Relative to manganese and nickel, cobalt has a lower propensity to migrate in a cubic-close-packed oxygen lattice, thereby offering the possibility of mitigating voltage fade
- Lithium extraction from a lithiated cobalt-rich spinel component, $\text{Li}_{2-x}\text{Co}_{2-2y}\text{Ni}_{2y}\text{O}_4$ ($0 \leq x \leq 1$), occurs at a significantly higher potential (~ 3.6 V) than a lithiated manganese-oxide spinel analogue, $\text{Li}_{2-x}\text{Mn}_2\text{O}_4$ (~ 2.9 V)

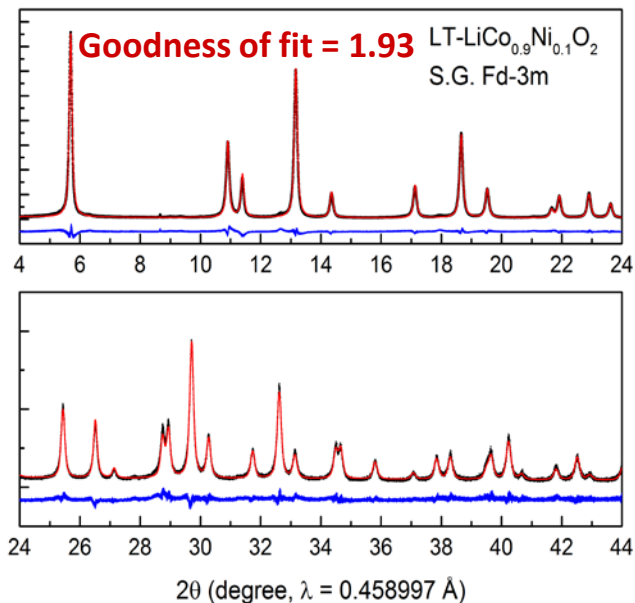
The Layered-Spinel LiCoO₂ Structural Anomaly



- The X-ray diffraction pattern of layered-LiCoO₂ with an ideal cubic-close-packed oxygen array with $R\bar{3}m$ symmetry ($c/a = 4.90$) is identical to that of a lithiated spinel structure, Li₂[Co₂]O₄ with $Fd\bar{3}m$ symmetry!

Rietveld Analyses of LT-LiCo_{0.9}Ni_{0.1}O₂ - synchrotron XRD data

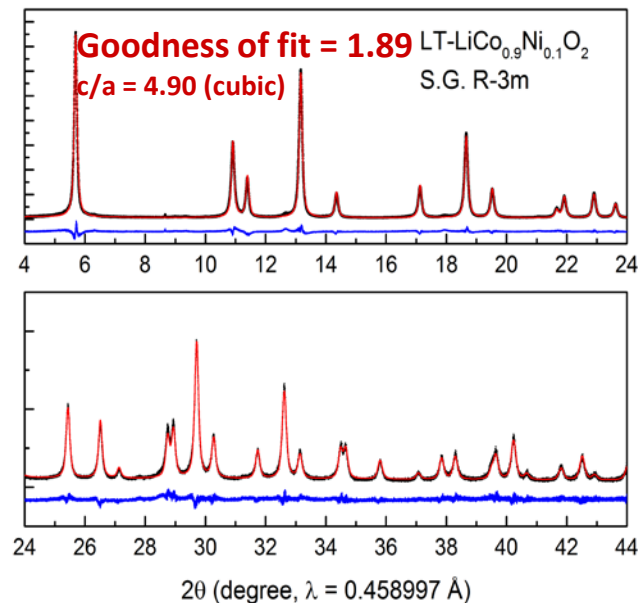
Spinel (Fd-3m) and Layered (R-3m) symmetry



Space group	<i>Fd-3m</i>					
Lattice constants (Å)	a = 8.007(4)					
$R_p / R_{wp} / R_{exp}$ (%)	6.85 / 9.28 / 4.81					
Goodness-of-fit	1.93					
Atom	Site	x	y	z	Occ.	B _{eq}
Li1	16c	0	0	0	0.97(6) [†]	0.38(6) [‡]
Li2	16d	0.5	0.5	0.5	0.02(4) [†]	0.38(6) [‡]
Co1	16d	0.5	0.5	0.5	0.97(6) [†]	0.38(6) [‡]
Co2	16c	0	0	0	0.02(4) [†]	0.38(6) [‡]
O	32e	0.259(7)	0.259(7)	0.259(7)	1	0.47(3)

[†]Occupancies of Li and Co were refined with a constraint that would satisfy the anti-site exchange condition.

[‡]B_{eq} of Li and Co was constrained to have the same value.



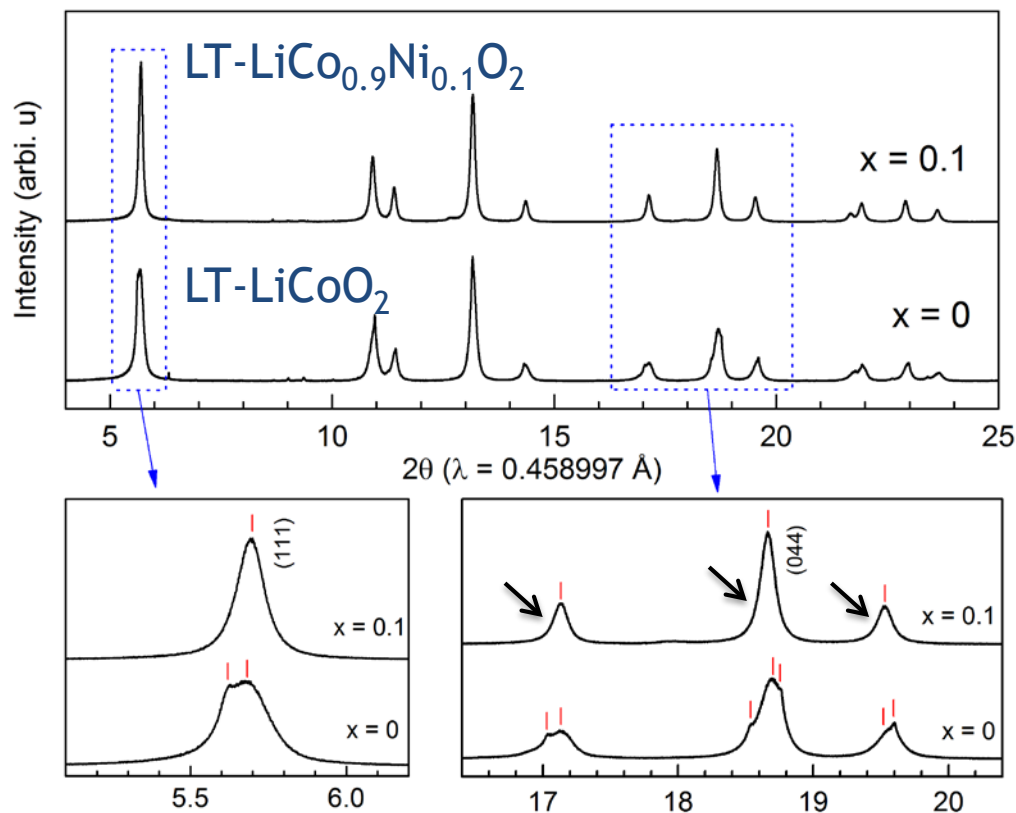
Space group	<i>R-3m</i>					
Lattice constants (Å)	a = 2.830(7), c = 13.872(3), c/a = 4.90					
$R_p / R_{wp} / R_{exp}$ (%)	6.83 / 9.11 / 4.81					
Goodness-of-fit	1.89					
Atom	Site	x	y	z	Occ.	B _{eq}
Li1	3a	0	0	0	0.98(3) [†]	0.33(1) [‡]
Li2	3b	0	0	0.5	0.01(7) [†]	0.33(1) [‡]
Co1	3b	0	0	0.5	0.98(3) [†]	0.33(1) [‡]
Co2	3a	0	0	0	0.01(7) [†]	0.33(1) [‡]
O	6c	0	0	0.240(3)	1	0.37(7)

[†]Occupancies of Li and Co were refined with a constraint that would satisfy the anti-site exchange condition.

[‡]B_{eq} of Li and Co was constrained to have the same value.

■ Lithiated spinel and layered structures are indistinguishable within experimental error

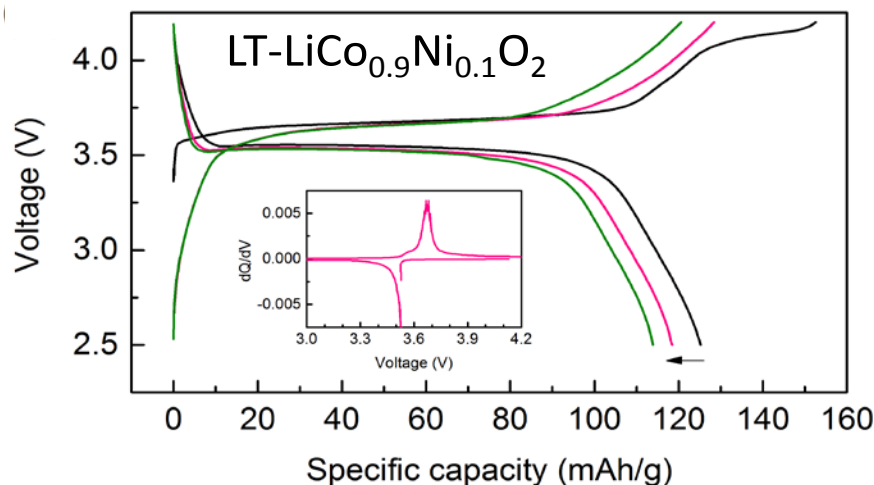
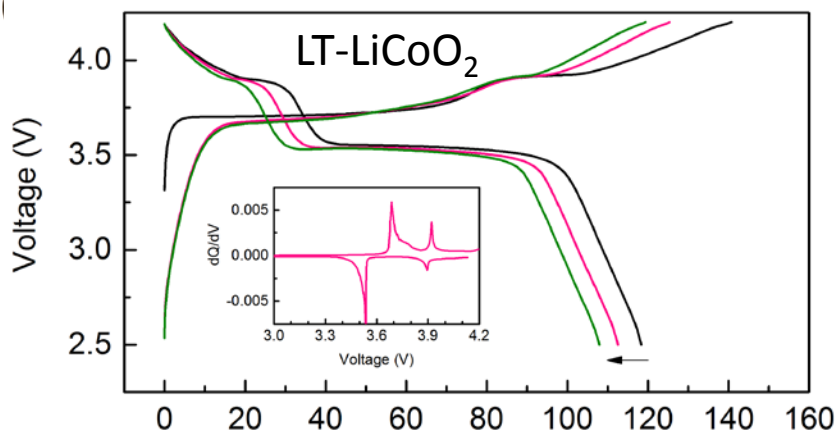
Synchrotron XRD patterns of LT-LiCo_{1-x}Ni_xO₂ (x=0 & 0.1)



- LT-LiCoO₂ (x=0, 400 °C) unequivocally contains lithiated spinel and layered components (peak splitting/broadening)
- LT-LiCo_{0.9}Ni_{0.1}O₂ (x=0.1, 400 °C) contains predominantly lithiated spinel; slight peak asymmetry suggests a small deviation from an ideal spinel distribution of cations
- Further analysis of LT-LiCoO₂ reported in **ES235** (Characterization/modeling project - Croy)

Electrochemical Profiles of Li/LT-LiCo_{1-x}Ni_xO₂ Cells

(Synthesis temperature: 400 °C)



- Electrochemical profile shows both layered behavior (~3.9 V) and lithiated spinel behavior (~3.5 V)
- Spinel cycling more stable than layered cycling \Rightarrow layered structure is metastable, not ideally configured
- 10% Ni substitution promotes spinel formation at 400 °C
- dQ/dV plot clean \Rightarrow cubic spinel and 'cubic-layered' structures
- Irreversible reaction at ~4 V on initial charge \Rightarrow unstable layered component?
- Efforts underway to integrate Co-based spinels into layered NMC structures

■ Invention Report/US Patent Application Filed on Further Advances

Future Work - FY2017/FY2018

- Good momentum has been gathered and progress made in advancing the performance of Li- and Mn-rich 'layered-layered-spinel' (LLS) cathode materials and stabilizing their surfaces through compositional control.
- High-potential (~ 3.5 V), lithiated Co- and Ni-based spinels have been evaluated as potential components for LLS electrode systems – this research has provided an encouraging new direction for this sub-project (not yet publicly disclosed).
- For the remainder of FY2017 and in FY2018, efforts will focus on optimizing the capacity, rate and electrochemical stability of LLS electrode materials.
- Collaborative interactions with industry to evaluate ANL's baseline LLS electrodes and surface-treated materials have been initiated.
- Complementary studies, both experimental and theoretical, to characterize bulk LLS and surface structures will be undertaken to gather information about the reasons for their electrochemical behavior (ES235)

Note: Any proposed future work is subject to change based on funding levels

Summary

- Recent trends:
 - Nickel-rich cathodes (NCA, 811, 622) are in vogue
 - Increasing the upper voltage cutoff (~ 4.4 V)
 - Safety concern (need non-flammable electrolytes)
- Layered-spinel composite structures hold promise to enhance the capacity and cycling stability of $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ (NMC) electrodes
 - Mn-rich (lower cost and toxicity)
 - Stabilizing Li in the TM layers (Li_2MnO_3)
 - Stabilizing TMs in the Li layers
 - Protective surface layers
 - Safer than Co-rich and Ni-rich electrodes

Acknowledgments

Support for this work from the BMR Program, Office of Vehicle Technologies, DOE-EERE, is gratefully acknowledged – Tien Duong, David Howell